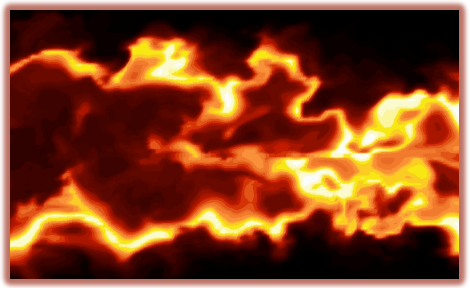
Imperial College London

MACCCR/AFOSR Fuel Research Review
Los Angeles, September 15-17, 2009.

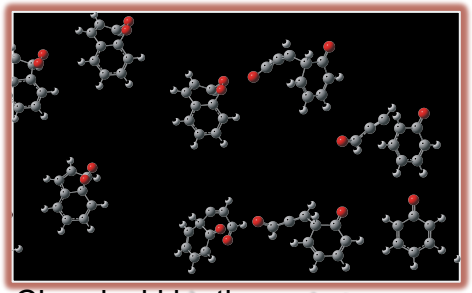
Detailed and Simplified Chemical Kinetics of Aviation Fuels and Surrogates

Prof Peter Lindstedt (PI), Mrs Valentini Markaki[1] (PhD Student) and Dr Roger Robinson (Research Fellow, Part Time)

[1]Supported by EOARD/AFOSR via Award FA8655-06-1-3052. Thanks are due to Dr Julian Tishkoff (AFOSR) and Dr Surya Surampudi (EOARD).



Turbulence chemistry interaction



Chemical kinetics

Imperial College London

Background

Technical Objective

- To develop detailed and simplified chemical mechanisms for surrogate fuels and to determine thermochemical data.

Approaches

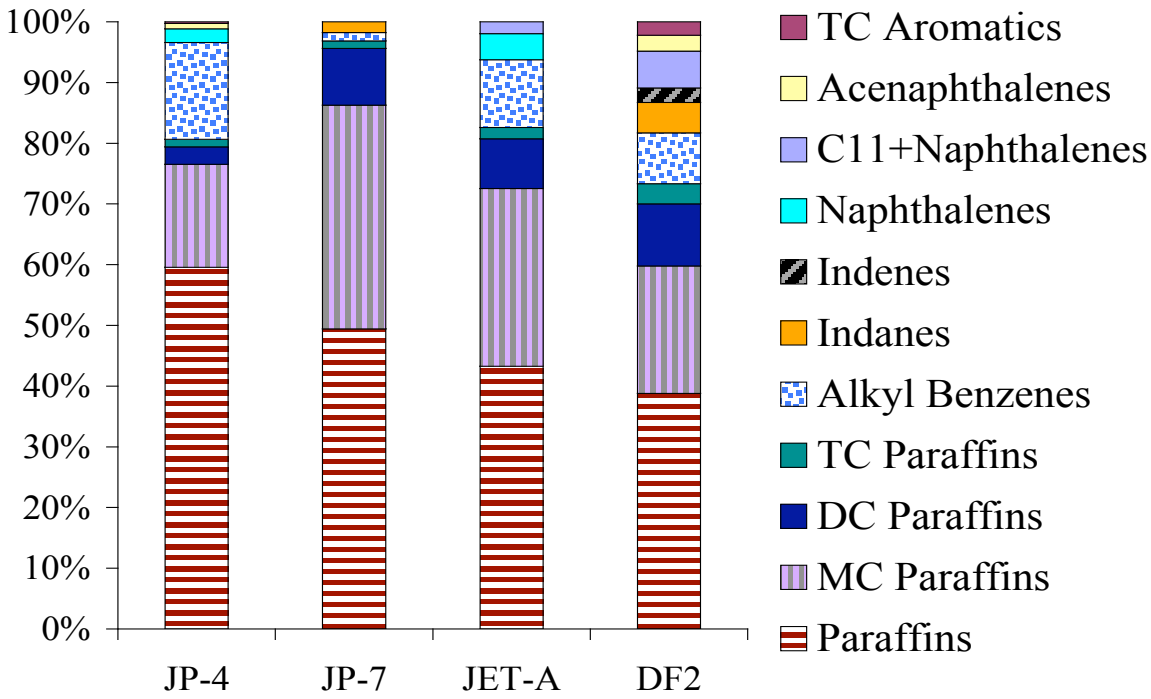
- Calculation methods based on quantum mechanical methods featuring RRKM/master equation and variable transition state techniques.
- Extensive validation wrt global properties and species concentrations.

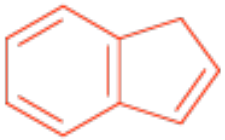
Cases Studied

- Systems covered include cyclopentadienyl pyrolysis/oxidation, the benzene/naphthalene and toluene/1-methyl naphthalene analogies as well as n-propyl benzene.

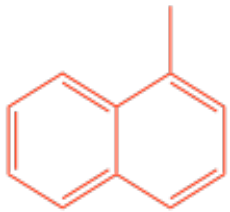
Imperial College London

Surrogate Fuels for Aviation Applications

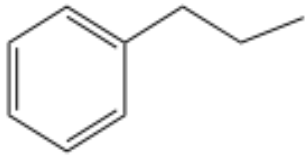




Indene



1-methyl naphthalene

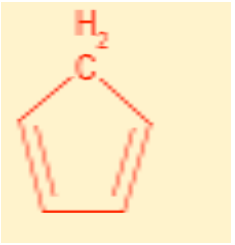


n-propyl benzene

C_nH_{2n+2}

alkanes

toluene



cyclopentadiene

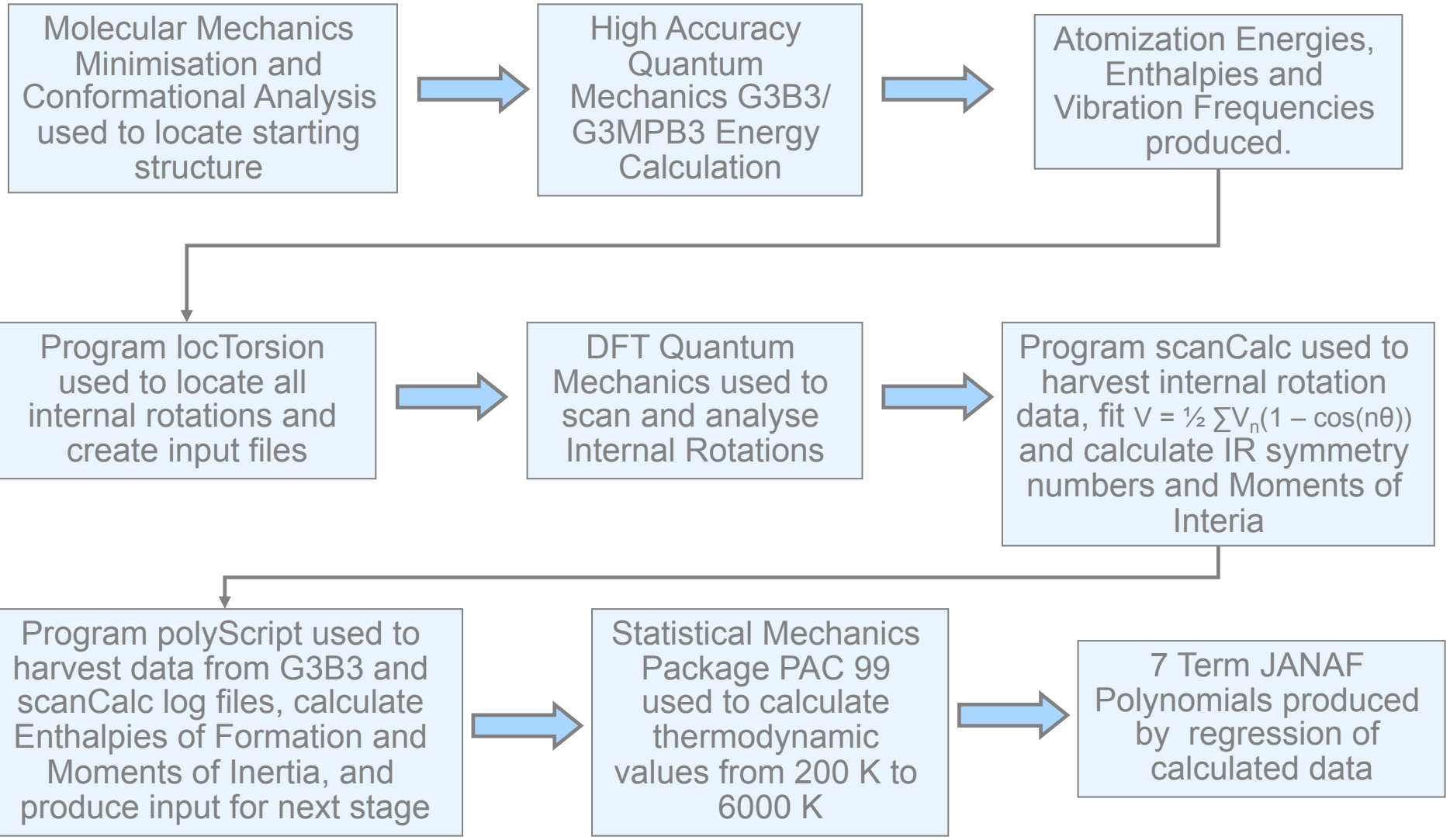
Imperial College London

Topics

- Progress on the oxidation and thermal decomposition of C_5-ring structures (e,g. Lindstedt, Maurice and Meyer, Proc. Roy. Soc. Chem. 2001; Lindstedt and Rizos, Proc. Combust. Inst., 2002; Lindstedt et al. 2009)
- Progress on the toluene/1-methyl naphthalene system – including some perhaps surprising sensitivites in the toluene auto-ignition process to issues in the hydrogen system (Gkagkas and Lindstedt 2009).
- Progress on the n-propyl benzene system and the application of an updated mechanism with new thermodynamic data derived using DFT and G3B3/G3MP2B3 composite quantum mechanical methods.
- Accurate thermodynamic data bases have been derived for 100+ chemical species relevant to the above systems.

Imperial College London

A Semi-Automated Method for High Quality Thermodynamic Data Determination



Imperial College London

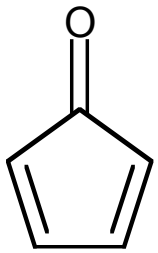
The Cyclopentadienyl System

- The cyclopentadienyl radical forms a key part of the main reaction pathway leading from single and multiple ring aromatics to linear hydrocarbons. The motivation was outlined at the MACCCR meeting in September 2008.
- Potential Energy Surfaces (PES) were calculated at the G3B3 level using Gaussian03 and compared to previous work (e.g. Zhong and Bozzelli 1998 and Kern et al. 1998).
- Reaction rates were calculated with a RRKM/Master-Equation approach using ChemRate. We also evaluated **POLYRATE** (Truhlar and co-workers).
- A detailed investigation of the C_5H_5 chemistry was performed and the impact of a substantial update featuring 21+ chemical reactions is evaluated here against experimental data from Butler (2001) and Butler and Glassman (2009).

Imperial College London

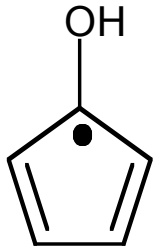
Examples from Thermodynamic Database

C5H4O



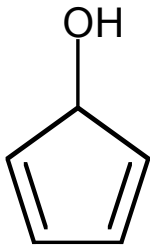
Calculated Data	
$\Delta_f H_{298}$	54.750
S_{298}	291.420
C_{p298}	84.202
$\Delta_f H_{1000}$	156.309

C5H4OH



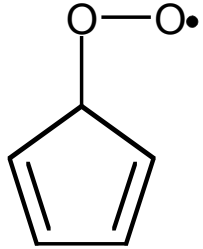
Calculated Data	
$\Delta_f H_{298}$	90.831
S_{298}	309.168
C_{p298}	95.931
$\Delta_f H_{1000}$	204.583

C5H5OH



Calculated Data	
$\Delta_f H_{298}$	-8.135
S_{298}	309.393
C_{p298}	100.137
$\Delta_f H_{1000}$	112.777

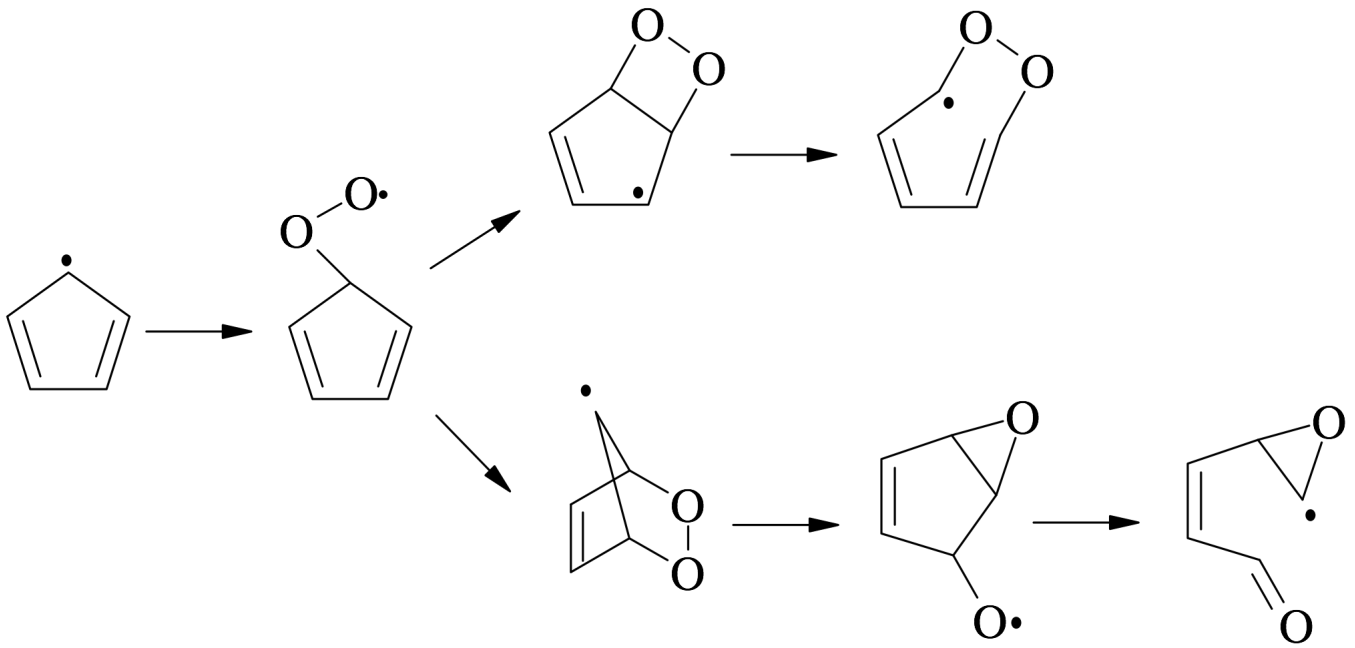
C5H5OO



Calculated Data	
$\Delta_f H_{298}$	215.590
S_{298}	352.445
C_{p298}	105.554
$\Delta_f H_{1000}$	338.507

Imperial College London

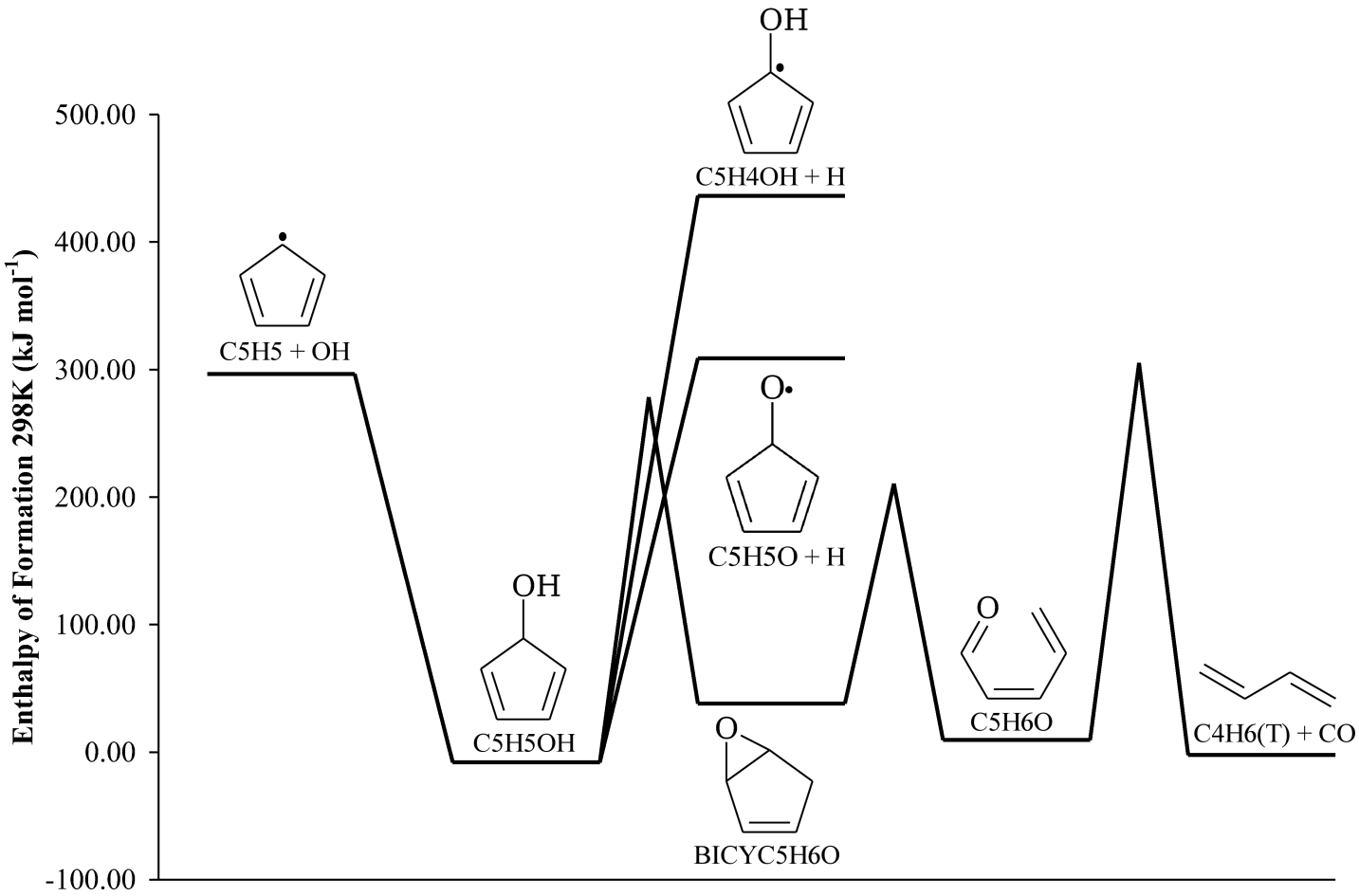
The Oxidation of PAH: Cyclopentadienyl Analog[1]



[1]R.P. Lindstedt, V. Markaki, R.K. Robinson, Oxidation of two-ringed aromatic species as models for soot surface reactions, Combustion Generated Fine Carbonaceous Particles, Ed. H. Bockhorn, A. D'Anna, A.F. Sarofim and H. Wang, Karlsruhe University Press 2009.

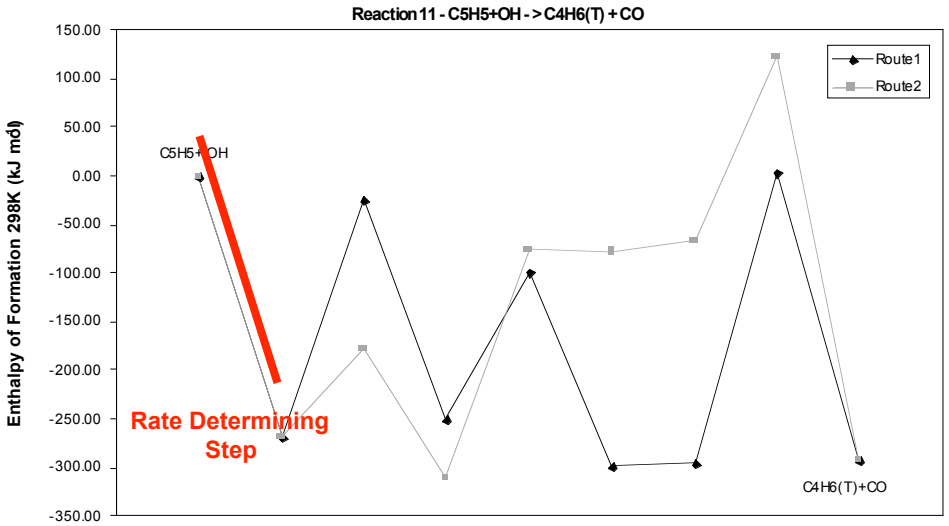
Imperial College London

Potential Energy for C_5H_5+OH Reactions



Imperial College London

Reaction 11 – C_5H_5 + OH → C_4H_6(T) + CO



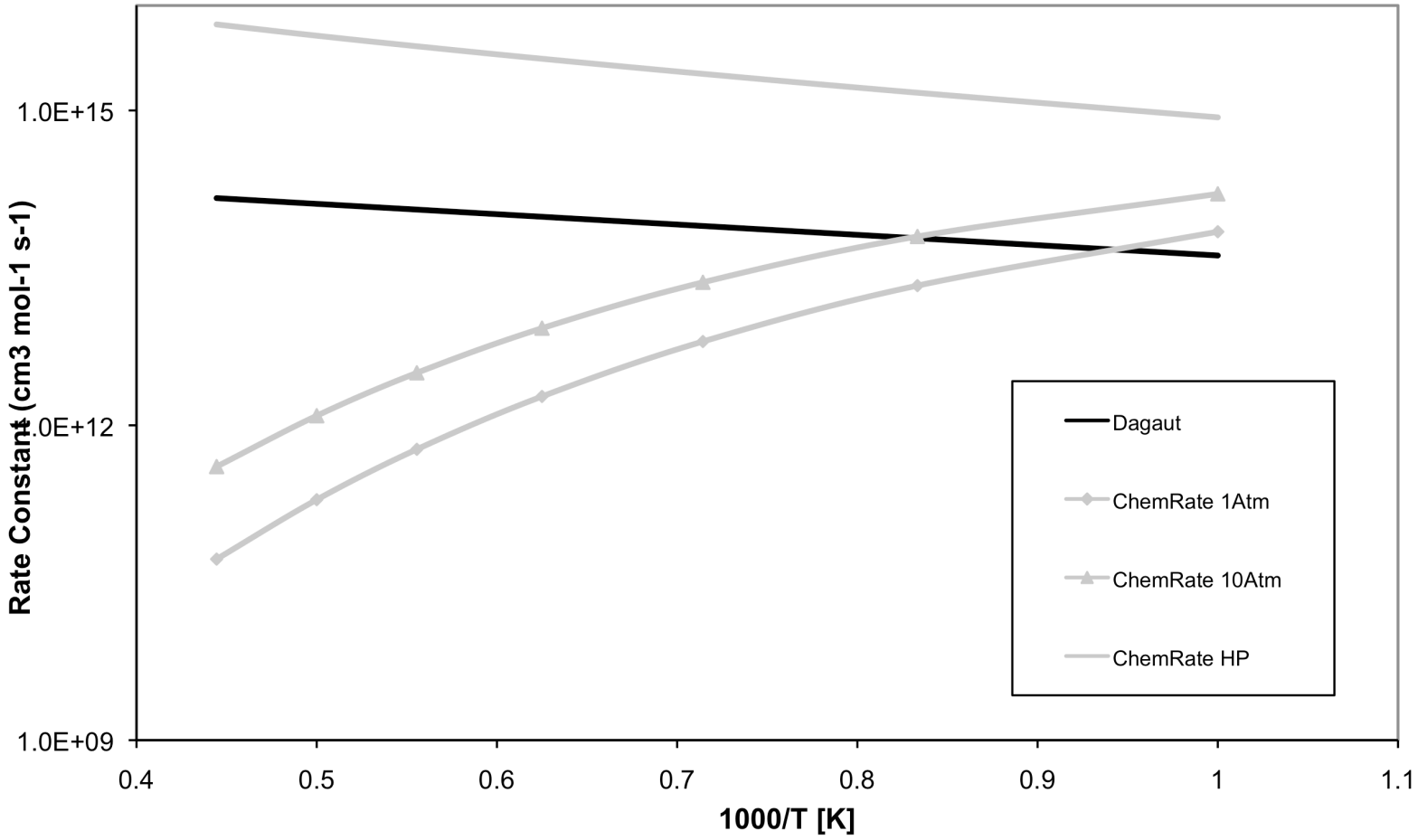
- No previous in depth study of the potential energy surface of this reaction.
- Two routes were explored for the breakdown of the C_5H_5 ring.
- Route 1 proceeded along a lower energy path and, as none of steps have a higher energy than the reactants, rates were calculated for the first step.

	Dagaut & Ristori	pw	pw	pw
	1 Atm	1 Atm	10 Atm	HP
A(cm3 mol^{-1} s^{-1})	4.00E +14	1.59E+66	6.41E+60	1.94E+12
n	0.00	-15.95	-14.11	1.17
Ea (kJ)	18.84	86.11	81.71	16.35

T	k	k	k	k
500	4.3E+12	1.4E+14	1.5E+14	5.4E+13
600	9.2E+12	2.4E+14	3.1E+14	1.3E+14
700	1.6E+13	2.4E+14	3.6E+14	2.4E+14
800	2.4E+13	1.8E+14	3.2E+14	4.1E+14
900	3.2E+13	1.2E+14	2.4E+14	6.1E+14
1000	4.1E+13	7.0E+13	1.6E+14	8.6E+14
1200	6.1E+13	2.1E+13	6.3E+13	1.5E+15
1400	7.9E+13	6.3E+12	2.3E+13	2.2E+15
1600	9.7E+13	1.9E+12	8.4E+12	3.1E+15
1800	1.1E+14	5.9E+11	3.2E+12	4.1E+15
2000	1.3E+14	2.0E+11	1.2E+12	5.2E+15

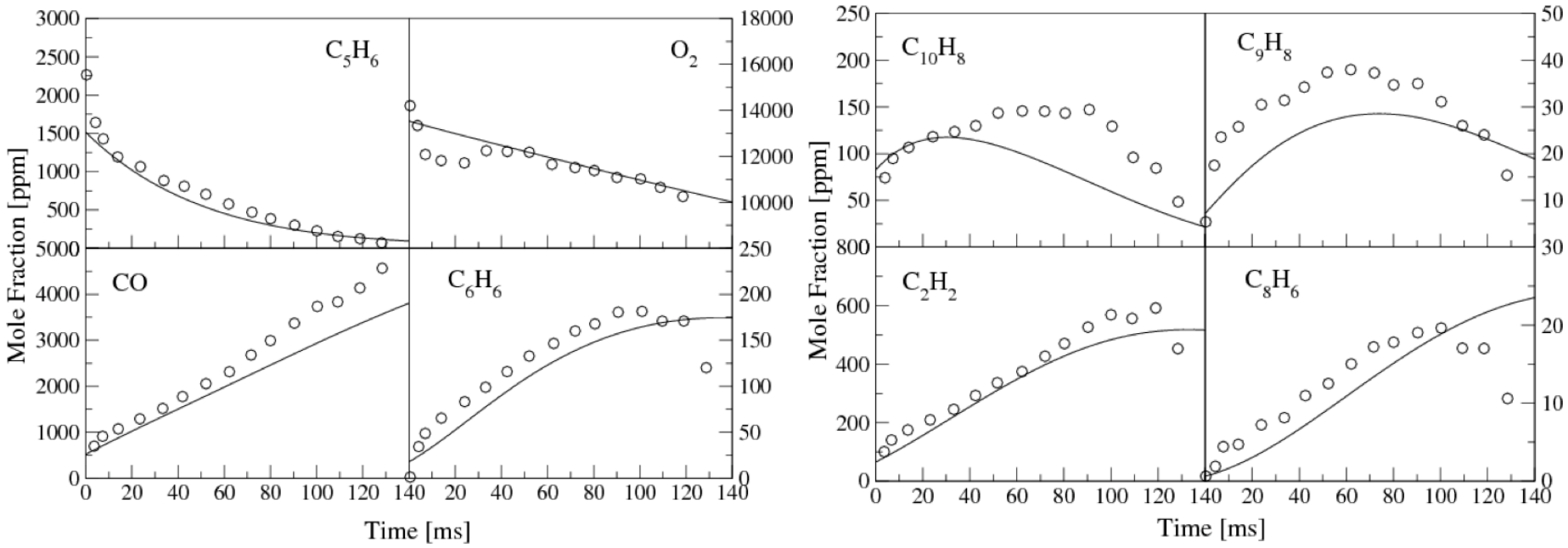
Imperial College London

Reaction 11 – C_5H_5 + OH → C_4H_6(T) + CO



Imperial College London

Cyclo-pentadiene Oxidation[1]

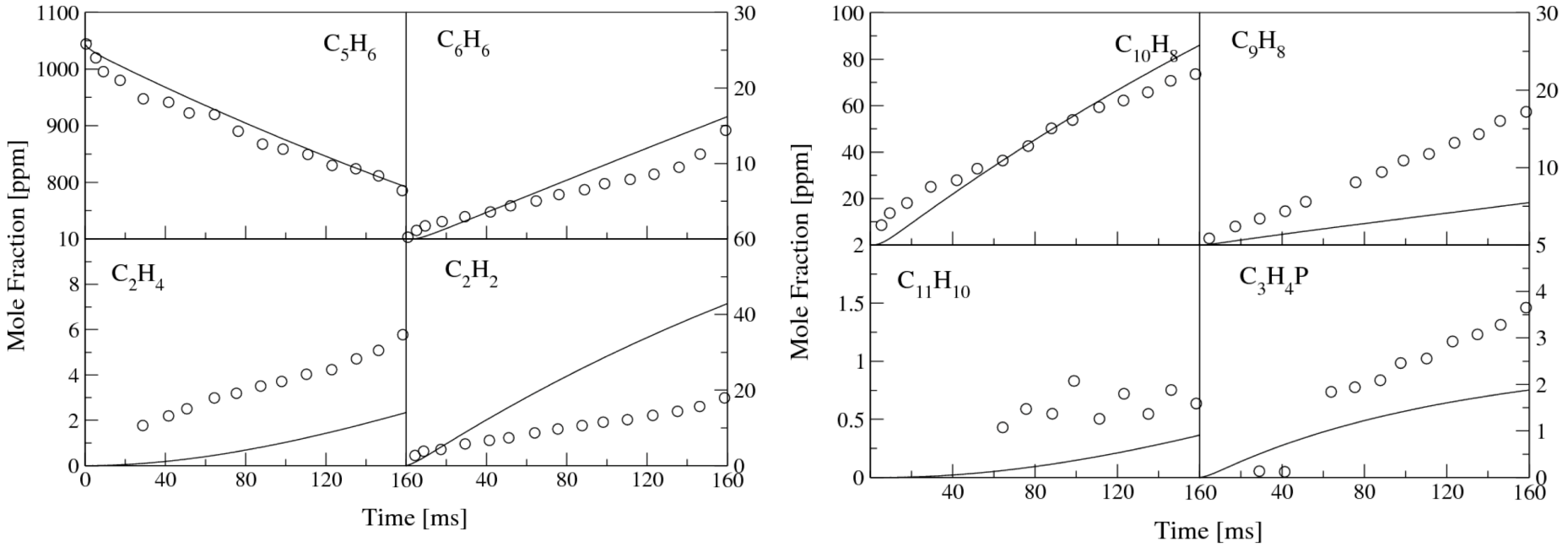


Concentration profiles during cyclo-pentadiene oxidation in a flow reactor. Φ = 1.03 (2243 ppm of fuel), P =1 atm, T = 1198 K. Circles are measurements (Butler and Glassman 2009) and solid line is current simulation.

[1]R.P. Lindstedt, V. Markaki and R.K. Robinson, Detailed Chemical Kinetics of Key Intermediates in the Oxidation of Aromatic Surrogate Fuel Components, Prepared for AFOSR/ARO Review Meeting on Chemical Propulsion, June 2009.

Imperial College London

Cyclo-pentadiene Pyrolysis

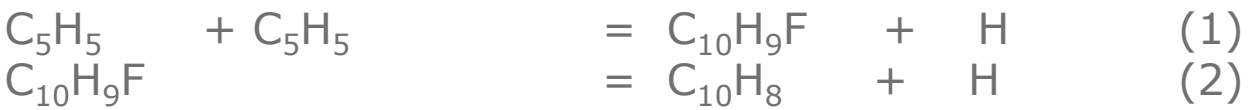


Concentration profiles during cyclo-pentadiene pyrolysis in a flow reactor (1044 ppm of fuel, P =1 atm, T = 1148 K. Circles are measurements (Butler and Glassman 2009) and solid line is current simulation.

Imperial College London

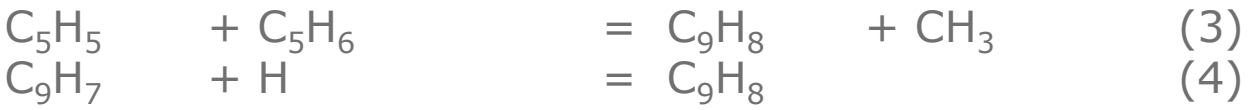
The Cyclopentadienyl PAH Growth

The major naphthalene growth pathway is via cyclopentadienyl radical recombination following the two-step sequence of Lindstedt et al. (2001) passing via the formation of $C_{10}H_9F$.



C_5H_5	+ C_5H_5	=	$C_{10}H_9F$	+	H	(1)
$C_{10}H_9F$		=	$C_{10}H_8$	+	H	(2)

For the pyrolysis cases, indene is formed predominantly via recombination of C_5H_5 and C_5H_6 with simultaneous methyl expulsion (3). The rate is based on the PES from the study by Wang et al. (2006).



C_5H_5	+ C_5H_6	=	C_9H_8	+ CH_3	(3)
C_9H_7	+ H	=	C_9H_8		(4)

For the oxidation cases, indene is predominantly formed via acetylene addition to the benzyl radical (5) with C_5H_6 and C_5H_5 recombination. The rate used is that of Colket et al. (1994), which was also analysed by Lindstedt and Maurice (1996).

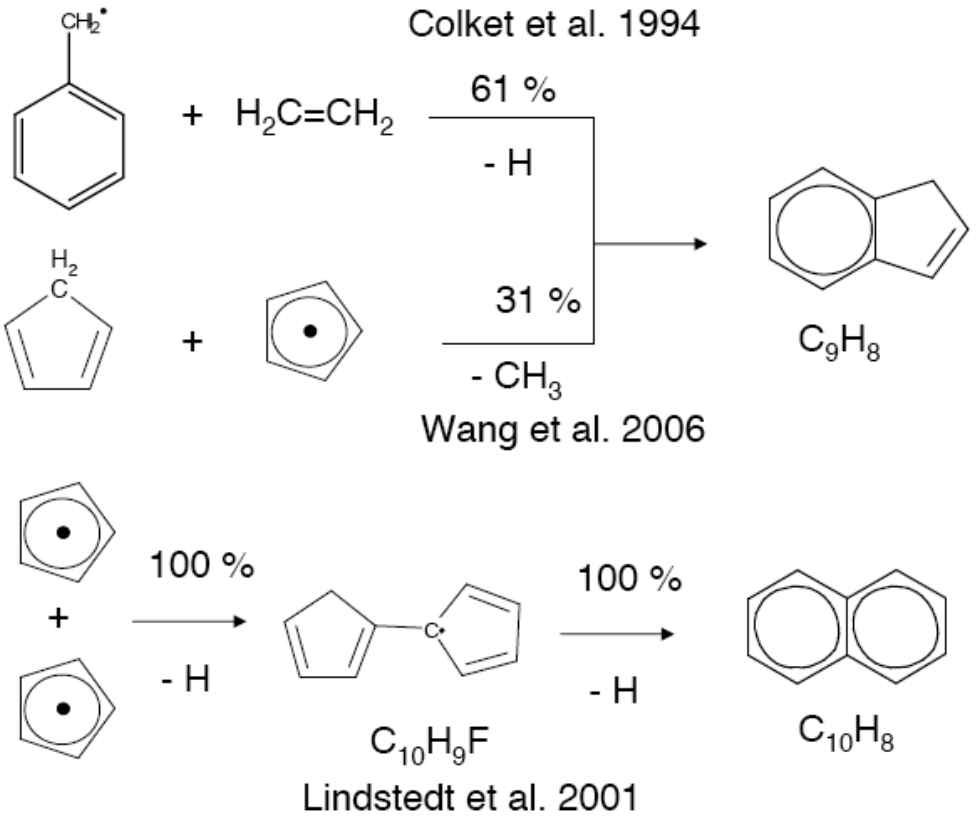
C_7H_7	+ C_2H_2	=	C_9H_8	+ H	(5)

Imperial College London

The Cyclopentadienyl PAH Growth

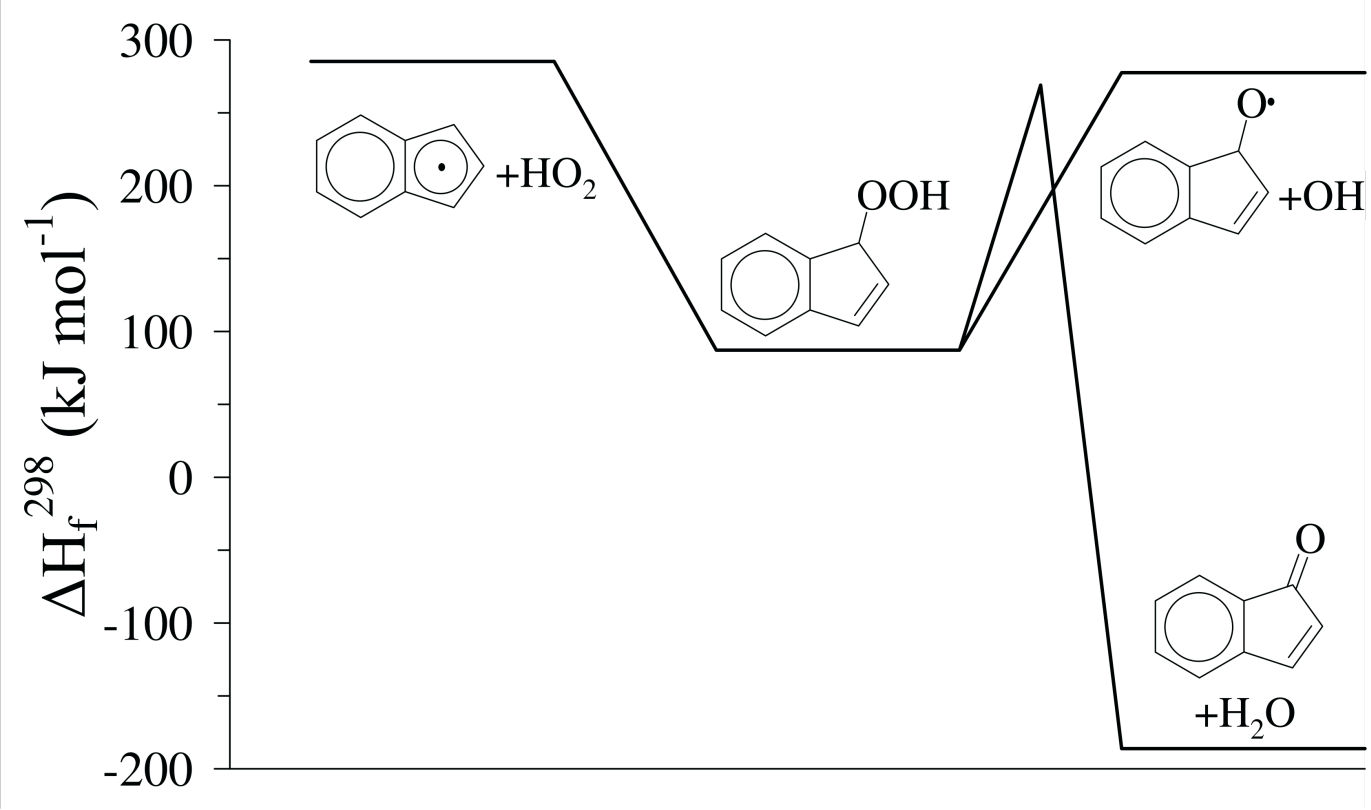
Major C_9H_8 and $C_{10}H_8$ formation channels for C_5H_6 oxidation in PFR (Phi = 1.6, T = 1153 K and initial fuel concentration = 2070 ppm).

Conditions used were obtained from Butler (2001).



Imperial College London

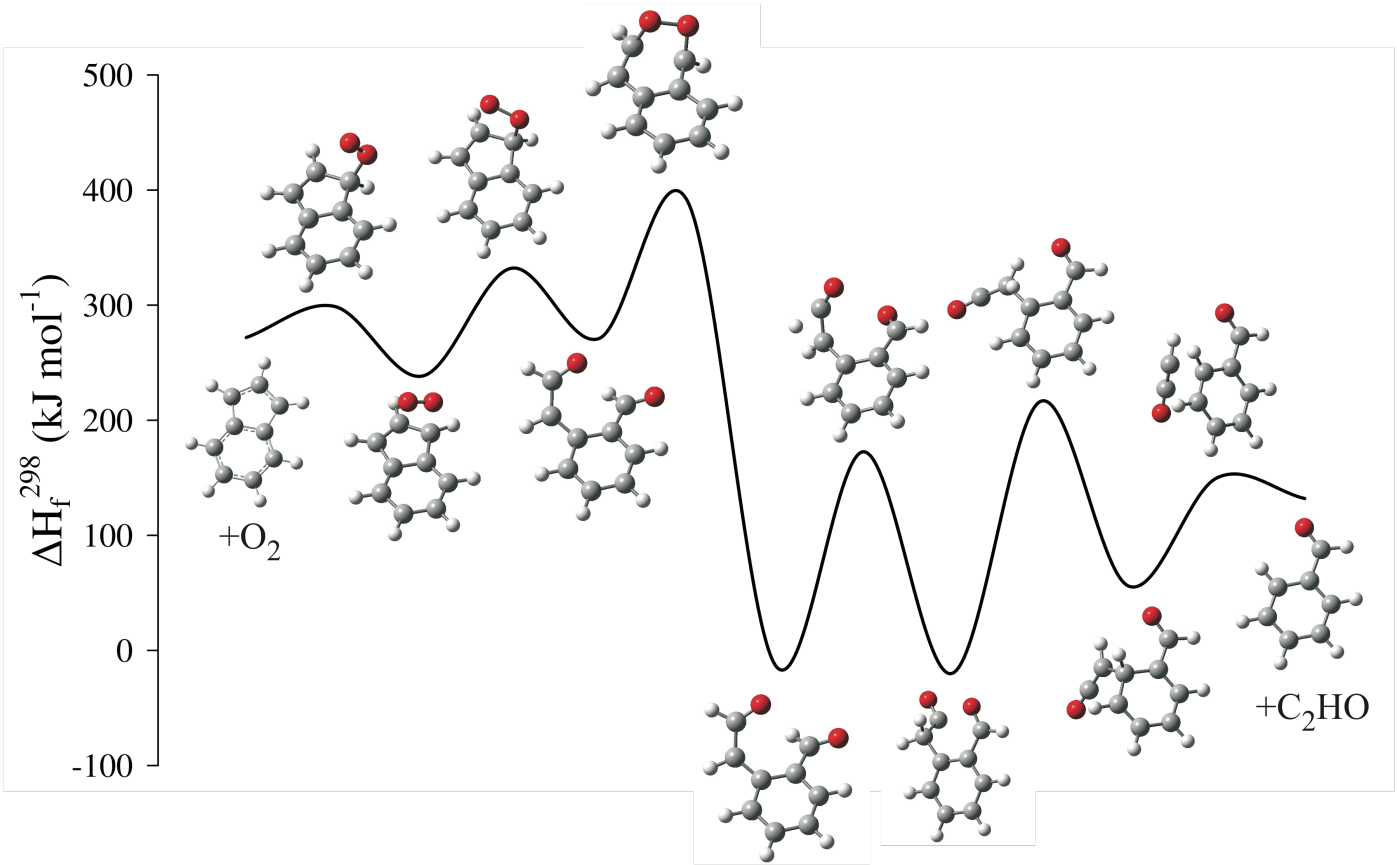
The Oxidation of Indene via HO_2 and O_2



[1]R.P. Lindstedt, V. Markaki, R.K. Robinson, Oxidation of two-ringed aromatic species as models for soot surface reactions, Combustion Generated Fine Carbonaceous Particles, Ed. H. Bockhorn, A. D'Anna, A.F. Sarofim and H. Wang, Karlsruhe University Press 2009.

Imperial College London

PES for $C_9H_7 + O_2 = C_7H_6O + HCCO$



[1]R.P. Lindstedt, V. Markaki, R.K. Robinson, Oxidation of two-ringed aromatic species as models for soot surface reactions, Combustion Generated Fine Carbonaceous Particles, Ed. H. Bockhorn, A. D'Anna, A.F. Sarofim and H. Wang, Karlsruhe University Press 2009.

Imperial College London

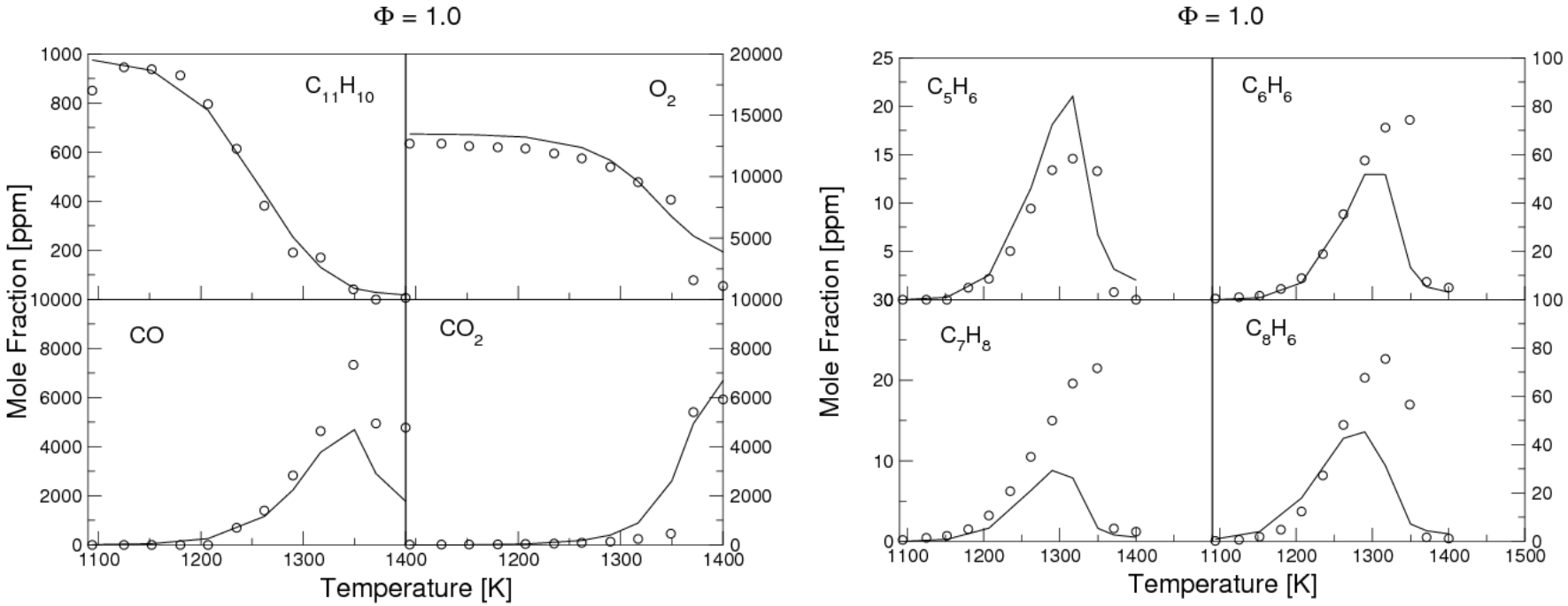
1-Methyl Naphthalene Oxidation

Φ	P (atm)	T (K)	XO_2	$XC_{11}H_{10}$
0.5	1.0	1097-1290	0.0270	0.001
1.0	1.0	1094-1400	0.0135	0.001
1.5	1.0	1147-1440	0.0090	0.001

- Concentration profiles during 1-methyl naphthalene oxidation in a jet-stirred reactor. In the subsequent graphs the circles are measurements (Mati et al. 2007) and the solid line the current simulation.
- Previous studies of 1-methyl naphthalene include those of Shaddix (1993), Pitsch (1996), Potter (2004), Mati et al. (2007).

Imperial College London

1-Methyl Naphthalene Oxidation[1]



Concentration profiles during 1-methyl naphthalene oxidation in a jet-stirred reactor. Φ = 1.0, P =1 atm, 1100 < T [K] < 1400. Circles are measurements (Mati et al. 2007) and solid line is current simulation.

[1]R.P. Lindstedt, V. Markaki and R.K. Robinson, Detailed Chemical Kinetic Modelling of Aromatic Diesel Fuel Components, Towards Clean Diesel Engines, June 2009.

Imperial College London

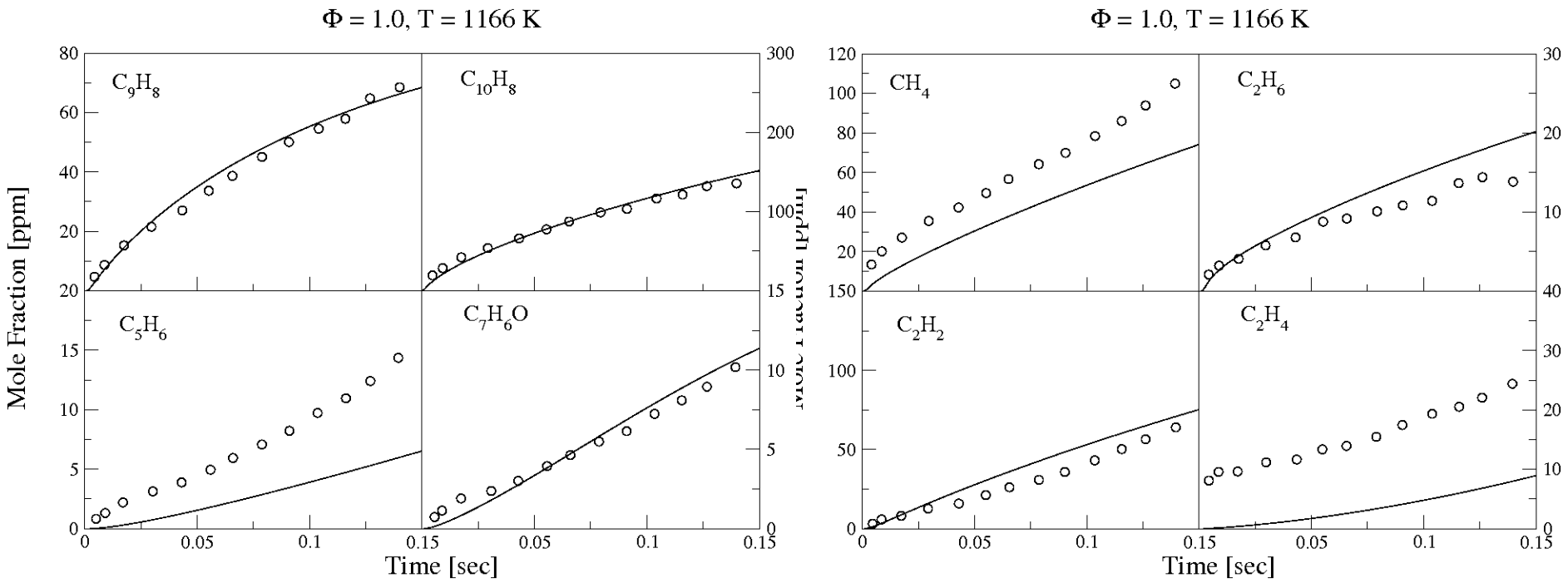
1-Methyl Naphthalene Oxidation[1]

Φ	P (atm)	T (K)	$[O_2]$ ppm	$[C_{11}H_{10}]$ ppm
1.0	1.0	1069	0.0270	0.001
1.5	1.0	1066	0.0135	0.001
1.5	1.0	1198	0.0090	0.001

Concentration profiles during 1-methyl naphthalene oxidation in a flow reactor. In subsequent graphs the circles are measurements (Shaddix et al. 1997) and the solid line the current simulation.

Imperial College London

1-Methyl Naphthalene Oxidation

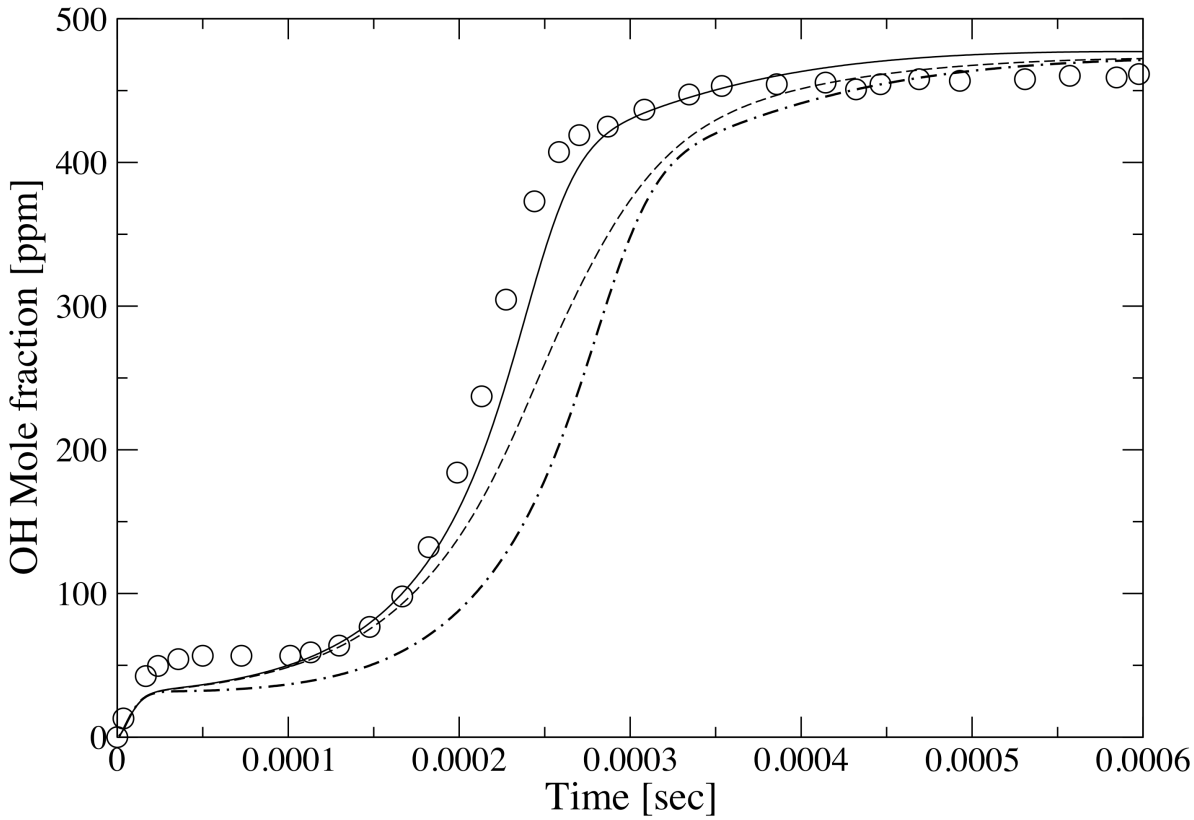


Concentration profiles during 1-methyl naphthalene oxidation in a flow reactor. The circles are measurements (Shaddix et al. 1997) and the solid line the current simulation.

Imperial College London

Toluene Chemistry

- Sensitivity analysis of the time resolved OH radical concentrations in Toluene/ Oxygen/Argon mixtures in shock tube with 0.1% toluene, 0.9% oxygen, T = 1689 K and P = 1.79 atm.
- Circles are measurements (Vasudevan et al. 2005).
- The solid line is our current model, the dashed line the same model with the rate of Baulch et al. (2005) for $O + H_2 \rightarrow OH + O$.
- The dashed dotted line is our current model with the $C_5H_5 + C_2H_2 \rightarrow C_7H_7$ channel removed.



Imperial College London

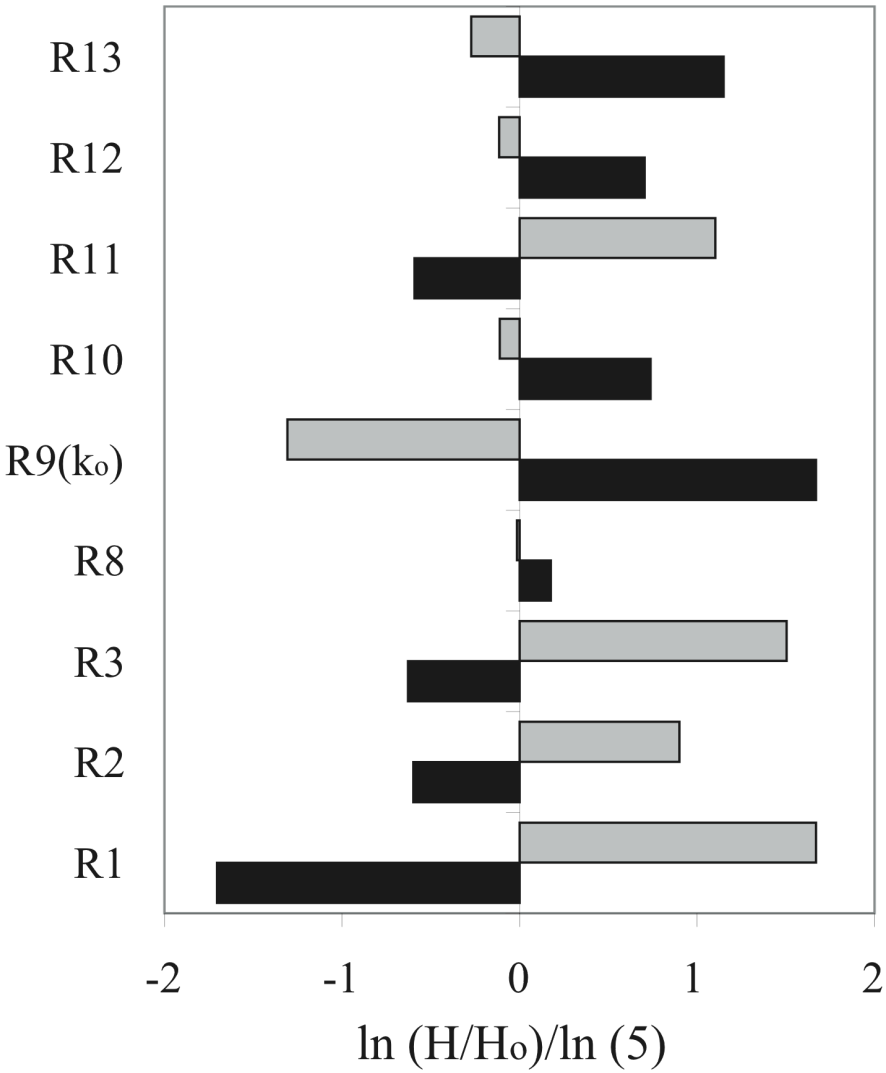
Hydrogen Chemistry

Number	Reaction	Li et al. [17]	Sun et al. [18]
1	$H + O_2 \rightleftharpoons O + OH$	6.97E+07	6.86E+07
2	$O + H_2 \rightleftharpoons H + OH$	2.83E+08	1.70E+08
3	$H_2 + OH \rightleftharpoons H_2O + H$	1.50E+09	1.60E+09
4	$O + H_2O \rightleftharpoons OH + OH$	5.90E+06	7.43E+06
5	$H_2 + M \rightleftharpoons H + H + M$	4.16E-10	1.92E-09
6	$O + O + M \rightleftharpoons O_2 + M$	1.91E+08	1.91E+08
7	$O + H + M \rightleftharpoons OH + M$	4.51E+09	4.51E+09
8	$H + OH + M \rightleftharpoons H_2O + M$	3.48E+10	2.02E+10
9	$O_2 + H + M \rightleftharpoons HO_2 + M\ k_0$	7.09E+10	6.61E+10
10	$HO_2 + H \rightleftharpoons H_2 + O_2$	1.12E+10	1.40E+10
11	$HO_2 + H \rightleftharpoons OH + OH$	6.13E+10	5.21E+10
12	$HO_2 + O \rightleftharpoons OH + O_2$	3.25E+10	2.02E+10
13	$HO_2 + OH \rightleftharpoons H_2O + O_2$	3.68E+10	1.86E+10

- Differences in reaction rates at 1045 K. The temperature was selected as characteristic in the turbulent flame ignition studies pursued by Gkagkas and Lindstedt (2009).
- The mechanism of Li et al. (2004) used the rate from Sutherland et al. (1986), which also formed the CEC recommendation of Baulch et al. (1992,1994), and Sun et al. (2007), used the more recent CEC suggestion of Baulch et al. (2005).

Imperial College London

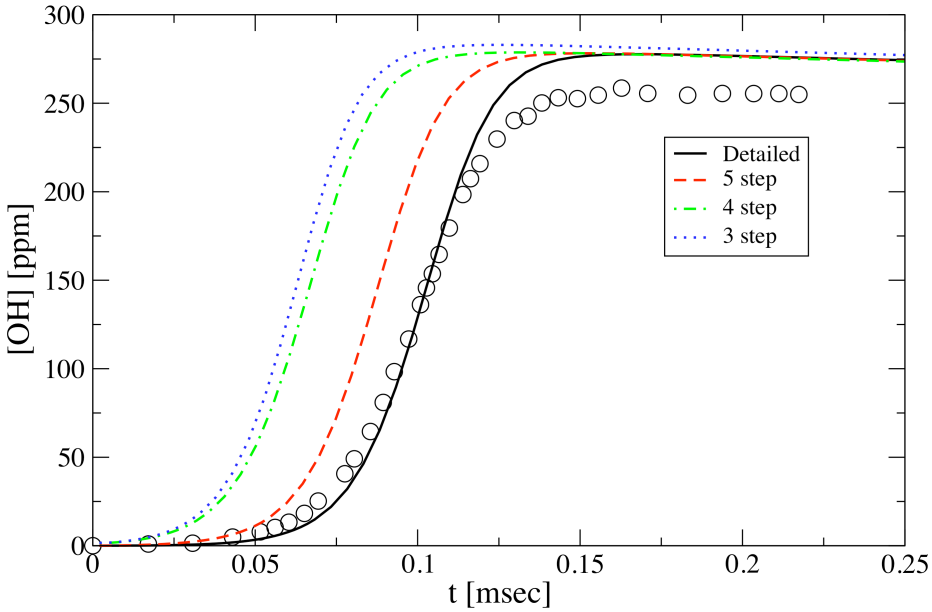
Background: Hydrogen Chemistry

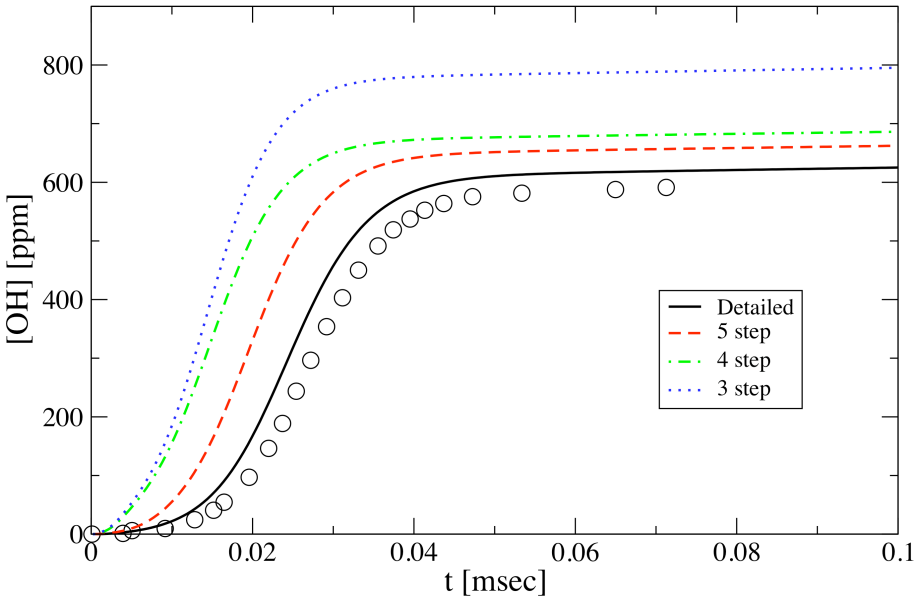


- Logarithmic sensitivities of the liftoff height to changes in reaction rate parameters.
- Reaction 2 has the unfortunate combination of sensitivity and uncertainty.
- Analysis performed at 1045 K and atmospheric pressure.
- There is a need for a careful determination of rates in this difficult regime.

Imperial College London

Hydrogen Chemistry: Impact of QSSA on Reaction Dynamics





- Time resolved OH concentrations of $H_2/O_2/Ar$ mixtures in shock tubes obtained with detailed and systematically reduced chemical mechanisms. Symbols are measurements [43] and lines are calculations. Initial conditions are: (a) H_2=5.0%, O_2=0.493% at 0.675 atm and 1980 K (b) H_2=1.10%,O_2=0.208% at 1.98 atm and 2898 K.

Imperial College London

Summary

- Critical reaction paths in the oxidation of aromatic surrogate fuel components have been analyzed and more accurate rates of reaction determined via *ab initio* methods.
- Good progress made on several system, including several of relevance to substituted aromatics.
- Thermodynamic data bases have been substantially updated for a wide range of compounds, currently 100+ species, and a semi-automatic technique has been formulated and evaluated.
- Alkanes and other components currently addressed via large working groups (e.g. AFRL Energy IPT (PI: Egolfopoulos, USC) and a MURI (PI: Dryer, Princeton) and the current work is complementary.